Thin-layer chromatography of N,N-disubstituted dithiocarbamates of nickel(II) and cobalt(II)

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ABSTRACT

The separation and chromatographic behaviour with different mobile phases of dithiocarbamates of Co(II) and Ni(II) is reported. The effects of the solvent strength and the amine from which the chelate is derived were studied. Slopes of the straight-line plot of R_M vs. log X_s (X_s = molar fraction of the more polar component in the mobile phase) showed the differences in the adsorption of the metal chelates.

INTRODUCTION

Separations of neutral dithiocarbamates (DTCs) using different chromatographic techniques have been reported [1,2]. However, there has not been much work on the TLC behaviour of dithiocarbamates.

In 1973, Galík [3] made a theoretical study of the chromatographic behaviour of metal chelates because practical studies had not been possible. Soundararajan and Subbaiyan reported the TLC of some DTCs of Zn, Cd and Hg [4] and the separation of Tl(I) and Tl(III) DTCs by TLC [5].

In this work, we studied the TLC behaviour of the DmetDTC (dimethyldithiocarbamate),

DetDTC (diethyldithiocarbamate), BmetDTC (N-benzyl-N-methyl dithiocarbamate), BetDTC (N-benzyl-N-ethyldithiocarbamate), DbenDTC (N,N-dibenzyldithiocarbamate), (+)EpDTC [(+)-ephedrinedithiocarbamate], (−)EpDTC [(−)-ephedrinedithiocarbamate), (+)ΨEpDTC [(+)-Ψ-ephedrinedithiocarbamate], (−)ΨEpDTC [(−)-Ψ-ephedrinedithiocarbamate) and BetOHDTC (N-benzyl-N-ethanoldithiocarbamate) of Co(II) and Ni(II) with different mobile phases: hexane, toluene, benzene, diethyl ether and their binary mixtures.

The adsorption process of the chelates with binary mobile phase may be studied following Galík's equation [3]:

$$R_M = (-m/n) \log X_s + C$$

where C is a constant that includes the influence of the active component in the mobile phase (S),
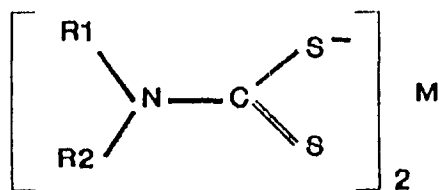
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the humidity and the temperature, X_s is the molar fraction of the active component S and m and n are the number of bonds with which the chelate and active solvent molecules, respectively, are adsorbed. Hence the slope $(-m/n)$ of the straight-line plot of R_M vs. log X_s is a measure of the degree of adsorption of chelate molecules.

EXPERIMENTAL

The sodium salts of dithiocarbamates were synthesized following the method suggested by Crovetto [6], Gómez [7] and Montes [8].

Thin layers (thickness 0.26 mm) were prepared by spreading a slurry of a mixture of 50 g of silica gel 60G (Merck, Darmstadt, Germany) and 120 ml of water with a Shandon multi-thickness applicator on clean glass plates (20 × 20 cm). In order to activate the layer for adsorption chromatography they were kept at 110°C for at least 90 min.

The samples were prepared by reaction of each ligand (sodium salts) with $CoSO_4 \cdot 7H_2O$ and $NiCl_2$ in aqueous medium up to saturation. The complex was extracted using ethyl acetate. The structure of the chelates studied is shown in Fig. 1.

The mobile phases (toluene–diethyl ether, benzene–diethyl ether and hexane–benzene of various compositions) were prepared just before use. The polarity of the solvents increases in order hexane < toluene < benzene < diethyl ether.

The plates were kept at 20°C and laboratory humidity until they were cold in order to obtain reproducible R_F measurements. The solution of metal chelate and ethyl acetate was spotted 2 cm from the lower end of the plates, which were then placed in saturated tanks (Shandon). The solvent front was allowed to move 15 cm from the spotted regions. The chelates were made visible with iodine vapour.

RESULTS AND DISCUSSION

The hR_F values (average of at least three experiments) are listed in Table I. These data and Figs. 2–4 [R_F values of Co(II) and Ni(II) DmetDTC vs. percentage of the more polar component in the mobile phase] demonstrate the metals can be separated under conditions used.

DmetDTC, DetDTC, BmetDTC and BetDTC show similar behaviour with respect to the metals. The resolution increases with increasing polarity up to toluene, then it decreases.

The behaviour of (+)EpDTC is the same as that of (−)EpDTC. In this instance the separa-

Dithiocarbamate derivative of	R_1	R_2
N,N-Dimethylamine (Dmet)	CH_3	CH_3
N,N-Diethylamine (Det)	$CH_2–CH_3$	$CH_2–CH_3$
N-Benzyl-N-methylamine (Bmet)	$CH_2–C_6H_5$	CH_3
N-Benzyl-N-ethylamine (Bet)	$CH_2–C_6H_5$	$CH_2–CH_3$
N,N-Dibenzylamine (Dben)	$CH_2–C_6H_5$	$CH_2–C_6H_5$
N-Benzyl-N-ethanolamine (BetOH)	$CH_2–C_6H_5$	$CH_2–CH_2OH$
(+)-Ephedrine [(+)Ep]	CH_3	$C_9H_{11}O$
(−)-Ephedrine [(−)Ep]	CH_3	$C_9H_{11}O$
(+)-Ψ-Ephedrine [(+)ΨEp]	CH_3	$C_9H_{11}O$
(−)-Ψ-Ephedrine [(−)ΨEp]	CH_3	$C_9H_{11}O$

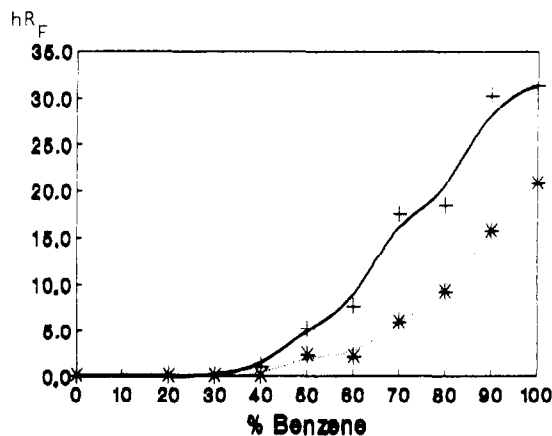Fig. 1. Structure of metal(II) N,N-disubstituted dithiocarbamates. M = Metal.

Fig. 2. Plots of hR_F versus percentage of benzene in the hexane–benzene binary mobile phase for (*) Co(II) and (+) Ni(II) DmetDTC.

TABLE I

R_F VALUES OF N,N-DISUBSTITUTED DITHIOCARBAMATES WITH BINARY MOBILE PHASES

Mobile phase	Composition	Metal	DTC								
			Dmet	Det	Bmet	Bet	Dben	(+)Ep	(−)Ep	(+)ΨEp	(−)ΨEp	BetOH
Benzene–diethyl ether	100:0	Ni	31.3	41.7	56.1	60.5	72.0	2.3	2.9	0.0	0.0	0.0
	90:10		63.7	72.1	75.3	77.1	79.2	27.8	30.1	6.9	7.5	2.5
	80:20		65.2	74.3	80.9	81.4	80.8	47.7	48.3	18.9	19.8	7.8
	50:50		70.7	77.2	82.2	83.0	84.0	65.8	71.7	52.9	51.0	23.6
	0:100							82.6	84.4	75.4	74.7	40.8
	100:0	Co	20.8	31.5	50.0	55.3	72.4	0.0	0.0	0.0	0.0	0.0
	90:10		62.2	75.1	78.2	79.7	80.7	9.1	9.1	1.0	1.6	0.0
	80:20		69.4	79.3	84.3	84.4	84.0	26.0	26.7	5.1	6.0	2.1
	50:50		72.4	82.3	84.6	85.2	86.1	61.7	71.0	31.3	28.7	10.4
	0:100							84.8	84.8	61.7	58.6	19.9
Toluene–diethyl ether	100:0	Ni	33.2	43.5	49.4	52.0	68.3	2.6	1.4	0.0	0.0	0.0
	90:10		43.3	64.7	70.3	77.0	83.2	22.1	24.0	4.1	4.9	1.1
	70:30		64.1	76.4	77.1	80.8	86.2	48.4	52.7	23.9	24.6	11.3
	50:50		66.7	74.4	83.8	83.9	87.4	62.8	68.5	43.2	44.3	21.8
	0:100		69.1					82.6	84.4	75.4	74.7	40.8
	100:0	Co	15.7	30.0	41.3	46.5	66.4	0.0	0.0	0.0	0.0	0.0
	90:10		43.9	63.7	72.0	78.9	85.4	4.7	4.9	0.0	0.0	0.0
	70:30		63.9	81.3	80.8	83.1	88.4	44.3	37.1	6.7	6.3	2.7
	50:50		65.1	79.7	84.9	85.1	90.5	56.3	60.3	20.6	21.3	8.4
	30:70		64.3					73.1	70.8	38.4	40.8	13.4
	0:100							84.8	84.8	61.7	58.6	19.9
Hexane–benzene[a]	80:20	Ni	0.0	1.7	0.6	3.0	6.3					
	60:40		1.0	7.5	6.7	14.4	19.9					
	40:60		7.8	21.5	20.8	29.8	40.5					
	20:80		18.5	33.3	43.1	48.5	63.7	0.0	0.0			
	0:100		31.3	41.7	56.1	60.5	72.0	2.3	2.9			
	70:30	Co	0.0	0.0	0.3	3.0	3.5					
	60:40		0.0	1.6	2.8	6.0	15.4					
	40:60		2.2	10.1	18.9	23.9	34.5					
	20:80		9.3	23.1	31.5	41.4	61.3	0.0	0.0			
	0:100		20.8	31.5	50.0	55.3	72.4	0.0	0.0			

[a] There is no mobility for (+)ΨEp, (−)ΨEp and BetOH with hexane–benzene as mobile phase.

tion occurs with higher solvent polarity, *i.e.*, with toluene–diethyl ether and benzene–diethyl ether binary mobile phases containing 10–50% of diethyl ether.

(+)ΨEpDTC, (−)ΨEpDTC and BetOHDTC have similar behaviour patterns. The resolution increases with increasing solvent strength from 20% of diethyl ether. There is no mobility with the mobile phase hexane–benzene.

N,N-Dibenzylamine derivatives show many differences from the other compounds studied. Low-polarity mobile phases such as hexane and

high-polarity mobile phases such as diethyl ether allow their separation.

With reference to N,N-substituents, the mobilities increase in the order DbenDTC > BetDTC > BmetDTC > DetDTC > DmetDTC > (+)EpDTC ⩾ (−)EpDTC > (+)ΨEpDTC ⩾ (−)ΨEpDTC > BetOHDTC.

The slopes of the R_M vs. log X_s plots are given in the Table II. The greater slopes of the Co(II) chelates with all types of mobile phase indicate their strong adsorption.
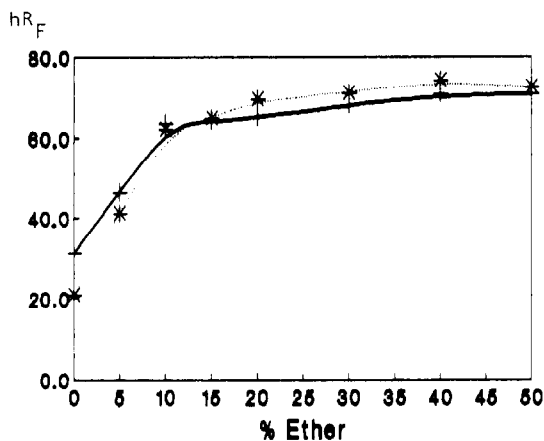
DTC molecules are adsorbed on the silica gel

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Fig. 3. Plots of hR_F *versus* percentage of diethyl ether in the benzene–diethyl ether binary mobile phase for (*) Co(II) and (+) Ni(II) DmetDTC.
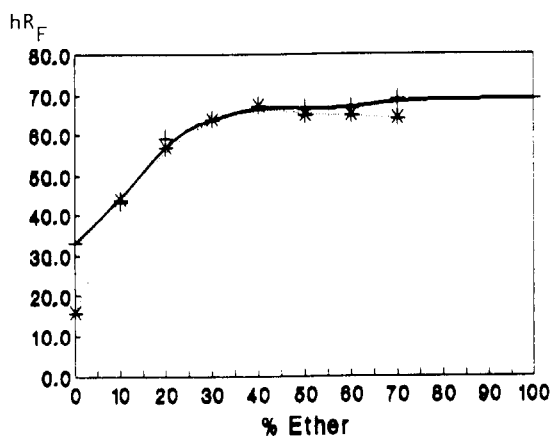

Fig. 4. Plots of hR_F *versus* percentage of diethyl ether in the toluene–diethyl ether binary mobile phase for (*) Co(II) and (+) Ni(II) DmetDTC.

TABLE III

BEST MOBILE PHASES SUGGESTED FOR THE SEPARATION OF N,N-DISUBSTITUTED DITHIOCARBAMATES OF Ni(II) AND Co(II)

Dimethyl-DTC	Toluene
Diethyl-DTC	Toluene
N-Benzyl-N-methyl-DTC	Hexane–benzene (20:80)
N-Benzyl-N-ethyl-DTC	Hexane–benzene (50:50 to 0:100)
N,N-Dibenzyl-DTC	Hexane–benzene (70:30)
(+)-Ephedrine-DTC	Benzene–diethyl ether (70:30)
(−)-Ephedrine-DTC	Benzene–diethyl ether (80:20)
(+)-Ψ-Ephedrine-DTC	Benzene–diethyl ether (60:40)
(−)-Ψ-Ephedrine-DTC	Benzene–diethyl ether (60:40)
	Toluene–diethyl ether (50:50)
N-Benzyl-N-ethanol-DTC	Diethyl ether

surface via the OH of the silica gel and the electron of the N atom of the thioureide. Also, the molecular area contributes to the adsorption of the chelate; if it increases, the adsorption of the molecule will decrease. However, (+)EpDTC, (−)EpDTC, (+)ΨEpDTC, (−)ΨEpDTC and BetOHDTC have an additional adsorbing site, namely the heteroatoms in their ligands, and thereby show lower R_F values in spite of their high molecular area. However, their mobilities increase with increasing polarity

TABLE II

SLOPES OF R_M *VERSUS* LOG X_s PLOTS FOR BINARY MOBILE PHASES WITH ACTIVE COMPONENTS DIETHYL ETHER AND BENZENE

Mobile phase	Metal	DTC									
		Dmet	Det	Bmet	Bet	Dben	(+)Ep	(−)Ep	(+)ΨEp	(−)ΨEp	BetOH
Benzene–diethyl ether	Ni	0.58	0.99	0.51	0.55	0.19	1.15	1.12	1.69	1.60	1.67
	Co	1.20	1.43	0.75	0.77	0.29	1.12	2.12	2.35	1.99	1.84
Toluene–diethyl ether	Ni	0.82	0.61	0.64	0.91	0.68	1.14	1.11	1.83	1.76	2.08
	Co	0.79	0.93	0.82	0.12	0.92	2.64	2.10	2.55	2.36	2.59
Hexane–benzene ether	Ni	4.57	3.71	3.88	3.14	5.08	1.38	1.65	−[a]	−[a]	−[a]
	Co	6.25	4.81	4.88	4.01	6.02	−[a]	−[a]	−[a]	−[a]	−[a]

[a] These R_M values are ∞.

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of the mobile phase. This variation is due to the mobile phase competing with the chelate molecules for the adsorption sites on the silica gel surface.

On the other hand, the R_F values of DmetDTC, DetDTC, BmetDTC, BetDTC and DbenDTC increase with increasing molecular area, but the polarity of the solvents only affects them up to one particular value and above this polarity the R_F values remains constant. Moreover, Ni(II) chelates, usually faster moving than Co(II) chelates, are found to be slower moving above this particular polarity. This variation in mobility shows the predominance of solubilizing properties over the adsorption characteristics of this chelates [5].

In conclusion, the conditions suggested are suitable for the separation of the Co(II) and Ni(II) chelates. The best separations can be achieved with the mobile phases indicated in Table III.

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